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(54) CHEMILUMINESCENT NITROGEN DETECTION METHOD AND APPARATUS

(71) We, ANTEK INSTRUMENTS, INC., a corporation organised and existing under the laws of the State of Texas, United States of America, of 6005 North Freeway, Houston, State of Texas, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a method and apparatus for the detection of chemically-bound nitrogen in samples utilizing chemiluminescent detection techniques.

The oldest and most widely used procedure for the analysis of chemically-bound nitrogen is the Kjeldahl method. Most often this method is used to obtain indirectly the protein content of foods and biological species. The method involves degradation and sulfation with heat, sulfuric acid and catalyst followed by neutralization, making strongly basic, distillation and titration of the ammonia. Sometimes many hours are required to perform this analysis, and there has recently been found evidence that people performing the Kjeldahl analysis on a daily basis run hazardous health risks.

Later, a titration device was devised which complemented the Kjeldahl method in that trace quantities of nitrogen could be determined accurately and quickly. This particular method involved a pyrolysis and hydrogenation of a sample at high temperatures and in the presence of a nickel catalyst. The resulting ammonia was coulometrically titrated using a four-electrode hydrogen cell. Systems based on these methods are better known as micro-coulometric titrating systems. Such an electrolytic titration apparatus is shown in the prior art as U. S. Patent No. 3,032,493 to D. M. Coulson, et al. However, certain disadvantages of coulometric titrating methods are apparent:

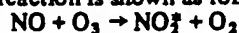
- (1). Ultra-high purity hydrogen is required;
- (2). A high degree of special analytical

techniques are necessary;

(3). Because of the use of hydrogen at high temperatures, there are certain questionable safety features of the method;

(4). A fairly low dynamic range is experienced. 50

More recently, chemiluminescent detection equipment for detecting chemically-bound nitrogen in the air has been developed. These chemiluminescent detectors are based on the reaction of nitric oxide with ozone for form metastable nitrogen dioxide (NO_2^*). Almost instantaneously the excited nitrogen oxide relaxes to its ground state with a resulting photo-emission (e). Such a reaction is shown as follows: 55



These chemiluminescent nitrogen detectors are commonly known as NO/NO_x detectors. These detectors are utilized to detect ambient nitric oxide and NO_x concentrations in the air for sampling techniques and pollution control as approved by the Environmental Protection Agency. Such NO/NO_x concentration meters are presently made by several companies, but they are limited in that they are able to detect chemically-bound nitrogen only as NO/NO_x gases using a chemiluminescent detection technique in gas samples or air samples. They cannot be utilized with liquid or solid organic compound samples. 60 65 70 75

In accordance with one aspect, the present invention provides a method for determining the total chemically combined nitrogen content of a sample, comprising the steps: 80

(a) decomposing said sample in one step in the presence of an oxygen-rich atmosphere of oxygen and an inert gas and at a temperature sufficiently above 700°C . that substantially all of the chemically bound nitrogen is converted to nitric oxide (NO), such decomposition being conducted in the absence of a catalyst, 85

(b) causing the nitric oxide produced by such decomposition to undergo a chemiluminescent reaction with ozone, and 90

(c) determining the magnitude of the chemiluminescent reaction to indicate the quantity of chemically combined nitrogen in said sample.

An advantage of the present method is that it may be used on samples that may be liquids or solids, as well as with gases, and is thus useful for determining the chemically combined nitrogen content of organic compounds. The present method is simple to operate and in preferred embodiment the results can be available in a matter of minutes.

The present invention also provides apparatus for determining the total chemically combined nitrogen content of a sample, comprising:

a furnace having an inlet for receiving a sample to be analysed and connected to sources of oxygen and an inert gas whereby substantially all of the chemically bound nitrogen in the sample can be decomposed in the furnace in the presence of an oxygen-rich atmosphere of oxygen and an inert gas to nitric oxide (NO);

a reaction vessel communicating with said furnace to receive the nitric oxide-containing decomposition product therefrom and communicating also with a source of ozone for chemiluminescent reaction with the nitric oxide received in the reaction vessel; and

chemiluminescent measuring means for determining the magnitude of a chemiluminescent reaction occurring in the reaction vessel to indicate the quantity of chemically combined nitrogen in said sample.

The method of the present invention may preferably be carried out by providing a source of an inert carrier gas, such as helium, or argon, a source of oxygen, and a furnace or pyrolyzing means connected to both of the sources of gases for receiving the carrier gas (helium or argon), the oxygen and the compound containing the chemically bound nitrogen. The furnace pyrolyzes the organic compound in an oxygen rich atmosphere at a temperature above 700°C to convert substantially all of the chemically-bound nitrogen to nitric oxide. The nitric oxide and carrier gas are applied to a drying means for drying the gas mixture in order to lower the dew point of the carried gases below a predetermined temperature level, which is less than the operating temperature of the reaction chamber. An ozone generator is provided for generating ozone from oxygen received from the oxygen source.

A chemiluminescent detecting means receives the nitric oxide and carrier gas from the drying means and the ozone from the ozone generator for mixing in a reaction chamber. The mixing of ozone and nitric oxide causes a chemical reaction resulting in photoemission of light energy. An optical filter is provided that passes light energy in the wavelength range of 600-900 nanometers for application to a photo-multiplier tube. The photo-multiplier tube of the detecting means generates an electrical potential proportional to the intensity of the emitted light energy.

The detector can further include an electrometer connected to the photo-multiplier to amplify and generate an analog electrical signal, in response to said electrical potential, representative of the received electrical potential. A recorder or other visual display or recording means is provided for receiving the analog electrical signal from the electrometer for recording. An integrating means is also provided to receive said analog electrical signal, for integrating signals representative of nitric oxide, and displaying on a digital counter a quantitative value proportional to the quantity of nitric oxide detected.

In certain applications, a gas chromatograph may also be utilized to receive the sample compound containing the chemically-bound nitrogen and the eg helium or argon carrier gas for chromatographically detecting elements other than nitrogen present in the compound. The helium and organic compound is then discharged into the pyrolysis furnace to pyrolyze and oxidize the organic compound to form nitric oxide for detection. Where a thermal conductivity detector is used in the gas chromatograph, elemental nitrogen may be detected.

In another embodiment, a gas chromatograph utilizing a flame ionization detector may be used. The oxygen and a source of hydrogen are applied to the flame ionization detector as well as the compound containing the chemically-bound nitrogen carried by the helium or other inert carrier gas except nitrogen. The flame ionization detector replaces the furnace in the preferred embodiment. However, excess water vapor must be removed from the carried gases by a moisture removing means and cooling means prior to application to the drying means and the detector reaction chamber.

Embodiments of the method and apparatus of the present invention will now be described in detail with reference to the accompanying drawings, in which:

Figure 1 is an electrical and mechanical schematic drawing of a chemiluminescent nitrogen detector according to a first embodiment of the present invention;

Figure 2 is an electrical and mechanical schematic drawing of a chemiluminescent nitrogen detector according to a second embodiment;

Figure 3 is an electrical and mechanical schematic of a chemiluminescent nitrogen detector according to a third embodiment;

Figure 4 is a graphical representation plotting the nitrogen detector response against furnace temperature in pyrolyzing chemical compounds to detect chemically-bound nitrogen;

Figure 5 is a graphical representation correlating quantitative values of nitrogen against the log of the integrator digital counter output of the nitrogen detector; and

Figure 6 is a sample or recording of the detector response in millivolts versus time showing

recorded peaks illustrating the detection of chemically-bound nitrogen in samples injected into the furnace.

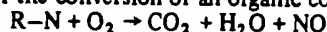
Referring now to Figure 1, a preferred embodiment of the chemiluminescent nitrogen detector is shown. The nitrogen detector is generally depicted by reference numeral 10, which comprises a helium source 12 connected by a pipe or tubing 13 through a flow meter 14, a tubing 15, and valve 16 as an input to a high temperature furnace 18. An oxygen source 20 supplies oxygen through tubing 21, flow meter 22, tubing 23, and valve 24 to a second input to furnace 18. A sample of compound containing chemically-bound nitrogen is inserted into the furnace to pyrolyze the organic compound in an oxygen-helium atmosphere and at a temperature above 700°C to form nitric oxide by a process that will be hereinafter further described. The pyrolyzed chemical compound including nitric oxide and carried by the helium is discharged from the furnace through line 25 to a drying means 26, and then through line 27 as one input to a reaction chamber 30 of the detector module 28. Oxygen from the oxygen source 20 is also applied through tubing 35 to an ozone generator 36. The ozone generator 36 generates a supply of ozone which is applied through tubing or line 37 as a second input to the reaction chamber 30 of the detector module 28.

In the reaction chamber 30, the mixing of nitric oxide with ozone causes a reaction that forms metastable nitrogen dioxide, which almost instantaneously relaxes to its ground state with a resulting photo-emission of light energy. The light emitted by the flameless reaction travels along path 38 through an optical filter 32 which passes only wavelengths of light energy in a predetermined wavelength range, namely 600-900 nanometers. The light energy traveling along path 38 exiting from optical filter 32 is applied as an input to a photo-multiplier tube 34. The photo-multiplier tube 34 receives electrical power from a terminal 42 which is applied via lead 43 to the tube. The photo-multiplier tube 34 receives the light energy travelling along path 38 and responds to the light energy by generating an amplified electrical potential proportional to the intensity of the light energy entering the photo-multiplier tube. The gas discharge from the reaction chamber 30 is applied through tubing 39 to an ozone scrubber 40, where the ozone is effectively scrubbed from the gases before the discharge gases are vented to the atmosphere through tubing 41.

The electrical potential generated by the photo-multiplier tube 34 is applied through electrical conductor 44 to an electrometer 46. The electrometer receives the electrical potential from the photo-multiplier tube 34 that is proportional to the intensity of the emitted light energy from the reaction chamber 30 and generates an analog electrical signal representa-

tive of the received electrical potential. The analog electrical signal generated by the electrometer is applied through conductor 53 to a chart recorder 54 or other conventional recording means for visually recording the analog electrical signal on a strip chart, or other visual indicating means. In addition, the output of the electrometer 46 is also applied via conductor 47 as one input to a voltage/frequency converter circuit 50 of the integrator module 48. The signal from the V/F converter 50 is applied through conductors 49 to a digital counter 52 for displaying a quantitative value on the counter proportional to the quantity of nitric oxide detected in detector module 28, and therefore proportional to the quantity of chemically-bound nitrogen in the organic chemical sample.

In order to analyze chemically-bound nitrogen, the sample must be converted to a detectable species. Such a conversion is accomplished in furnace 18 which subjects the sample to a very high temperature in an oxygen rich atmosphere. It has been found that the optimum ratio of oxygen to inert carrier gas, i.e., helium, as utilized in this embodiment of the present invention, is 6.5 to 1. The helium merely acts as an inert carrier vehicle for carrying the nitric oxide which is used as the detectable species of nitrogen available for detection of the chemically-bound nitrogen in the sample. The oxygen is utilized in the furnace with the compound containing the chemically-bound nitrogen to provide a source of oxygen to accomplish the conversion to nitric oxide during pyrolysis, illustrated by the following equation for the conversion of an organic compound:



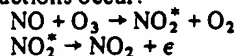
The nitric oxide (NO) becomes the detectable species of nitrogen for detecting the chemically-bound nitrogen in the organic compound sample.

As may be seen in Figure 4, at temperatures under 600°C, no ignition or conversion of the chemically-bound nitrogen (R-N) occurs as is shown in the area of the graph indicated by reference numeral 90. In the range of furnace temperatures between 600°-700°C, there is an area of explosive ignition or conversion as indicated by reference numeral 92. Above 700°C there is an area of smooth ignition or conversion of the chemically-bound nitrogen (R-N) to nitric oxide as indicated by curve 94. It may be seen from the graph, and it was experimentally determined, that optimum conversion of the chemically-bound nitrogen to nitric oxide occurs above 900°C, and may be seen on that portion of curve 94 as indicated by reference number 95. Also, at 900°C or higher no conversion of the chemically-bound nitrogen or nitric oxide to either nitrogen dioxide (NO₂) or nitrous oxide (N₂O) could be detected. Since it has been determined that the optimal conversion of the chemically-bound nitrogen to nitric oxide occurs above 900°C, a quartz

reaction tube is utilized as furnace 18. The quartz tube can operate continuously at such high temperatures necessary to convert the chemically-bound nitrogen to nitric oxide.

- 5 A highly desirable expedient concerning treatment of the sample before entering the detector 28 is that of moisture removal. Moisture removal from the nitric oxide and carrier gas, is accomplished by means of drying means
- 10 26. Drier 26 functions to receive the nitric oxide and helium mixture, dries the mixture by removal of water vapor, and lowers the dew point of the carried gases below a predetermined temperature level, a level that has been determined should not exceed the operating temperature of reaction chamber 30. If a higher dew point of the gases is allowed, the gases and water vapor would temporarily fog the window of the reaction chamber 30 with resulting blockage
- 20 of light to photo-multiplier tube 34. In practice it has been found that a desiccant such as magnesium perchlorate is very efficient, however, any other suitable desiccant or drying material could be utilized. The magnesium perchlorate has been found to have no noticeable nitric oxide absorption, which is important.

The detector module 28 houses a reaction chamber 30, where the ozone and nitric oxide are mixed to cause the chemiluminescent reaction. The chemiluminescent detection is based on the reaction of nitric oxide with ozone to form metastable nitrogen dioxide (NO_2^*). Almost instantaneously the excited nitrogen dioxide relaxes to its ground state with a resulting photo-emission (e). The following reactions occur:



Since the basic detector unit of the detector module 28 is a photo-multiplier tube 34, the response curve of the output of the photo-multiplier tube 34 is not linear. The response is logarithmic which requires a calibration curve to correlate the output of the counter 52 of the integrator 48 to a quantitative value of chemically-bound nitrogen detected in the sample. Such a calibration curve is shown in Figure 5 and is indicated by reference numeral 96.

A typical chart recording of chemically-bound nitrogen detected in samples is shown in Figure 6. The chart records millivolts of response versus time. The recording pin base line curve is shown at 98, and detected chemically-bound nitrogen in samples is shown at peaks 99 and 100. The counts shown on counter 52 of integrator 48 actually reflect a measure of the integration of the area under peaks 99 and 100 (see Figure 6) as a quantitative value proportional to the quantity of chemically-bound nitrogen present in the sample. As previously mentioned, such a correlation of quantitative value shown by counter 52 to quantitative values of nitrogen in the sample are shown in a typical correlation graph or curve shown in Figure 5.

A second embodiment of nitrogen detector 60 which may be used for conducting the present method is shown in Figure 2. In this embodiment of the nitrogen detector, the carrier gas source 12 (helium) is connected by tubing 13 through a flow meter 14, tubing 15, and valve 16 to the input of a gas chromatograph 62. The sample is introduced into the gas chromatograph in conventional manner, and a chromatographic analysis of the gases in the sample may be performed utilizing thermal conductivity detection. Of primary interest is the chromatographic detection of the presence of elemental nitrogen, such as, in the analysis of air pollutants containing chemically-bound and elemental nitrogen. The output of the gas column of the chromatograph 62 is applied through tubing 63 to introduce the sample gases to the input of furnace 18. Furnace 18 is identical to furnace 18 hereinabove described with regard to Figure 1, and will not be further discussed. Oxygen is supplied from oxygen source 20 through tubing 21, flow meter 22, tubing 23 and valve 24 as an input to the furnace 18 for providing an oxygen rich atmosphere for maximum conversion of the chemically-bound nitrogen in the sample to nitric oxide, as hereinabove described with regard to Figure 1. The remaining portions of the schematic shown in Figure 2, namely the application of the nitric oxide and its carrier gas, helium, as applied through drier 26 to the detector module 28, the generation of ozone by ozone generator 36 from oxygen from oxygen source 20, and application of the ozone to the detector module 28 are identical to the functions performed by the blocks having the identical reference numbers and therefore will not be hereinafter further described. The ozone scrubber 40 also performs the identical function as the ozone scrubber discussed with regard to the first embodiment shown in Figure 1.

The function of the reaction chamber 30, optical filter 32, and photo-multiplier 34 are identical to the functions of the identically referenced units of detector module 28 as hereinbefore described with regard to the first embodiment shown in Figure 1 and will not be further elaborated on herein. Similarly, the application of the photo-multiplier tube 34 output through electrometer 46, the recording of the electrometer output by recorder 54, and the integration and display of the electrometer output by integrator 48 and counter 52 are identical to the functions hereinabove described regarding the first embodiment as shown in Figure 1 and need not be further described.

In Figure 3, a third embodiment of a suitable nitrogen detector 70 is shown. Nitrogen detector 70 comprises a carrier gas source 12 which applies carrier gas helium through line 13, flow meter 14, tubing 15, valve 16, and tubing 73 to the input of a chromatograph column 75 of a gas chromatograph 72. The sample is introduced

through 74 into the chromatograph column 75. The output of the chromatograph column 75 is applied as an input to a flame ionization detector 76. Oxygen from oxygen source 20 is applied through tubing 21, flow meter 22, tubing 23, valve 24, and tubing 77 as a second input to the flame ionization detector 76. In addition, hydrogen from hydrogen source 78 is applied through line 79, flow meter 80, line 81, valve 82, and tubing 83 as a third input to the flame ionization detector 76. Flame ionization detector 76 may be of any conventional gas chromatograph flame ionization detector. Pyrolysis of the chemical compound carrying the chemically-bound nitrogen occurs in flame ionization detector 76, thus eliminating the need for furnace 18 as shown in previous two embodiments illustrated above in Figures 1 and 2.

The output of the flame ionization detector 76 now containing nitric oxide, other gases and the helium as a carrier is applied through tubing 85 as an input to a water vapour removal means 86, which may conveniently be a water trap, for removing water vapor from the carried gases. A cooling means 88 is provided to cool the hot gases and cause the water vapor to condense in the moisture trapping means 86. The output of the moisture trap 86 is through a tubing 89 as an input to a conventional drying means 26. The drying means 26 is identical to the drying means 26 illustrated in Figures 1 and 2 with regard to the first two embodiments and need not be further described. The output of the drying means 26 is applied through a tubing 27 as one input to reaction chamber 30 of the detector module 28. The ozone generator 36, ozone scrubber 40 and detector 28 are identical to those units hereinabove described with regard to previous embodiments shown in Figures 1 and 2, and need not be further described. Similarly, the recording and display electronics comprising electrometer 46, recorder 54, and integrator 48 all function in an identical manner to their counterparts of same reference number shown in Figures 1 and 2 and need not be herein further described.

In the preferred embodiment of Figure 1, the various modules and units identified in the block diagram can conveniently be comprised of the following commercially available equipment:

Furnace 18	-----	Antek Instruments, Inc.
Ozone generator 36	-----	Model 771 pyro-reactor
Ozone scrubber 40	-----	McMillan Electronics Corp. Part no. 1200350
Detector module 28	-----	McMillan Electronics Corp. Part no. 0045
	-----	McMillan Electronics Corp. Detector assembly of model 2200
V/F Convertor 50	-----	NO/NO _x meter
	-----	Burr Brown Co. No. VFC-12
Counter 52	-----	Antek Instruments Inc. Part no. 1893A

Electrometer 46 ----- McMillan Electronics Corp. Part no. 210-052

Of course, other suitable conventional circuits and apparatus may be substituted for the blocks of the block diagrams of Figures 1-3. WHAT WE CLAIM IS:-

1. A method for determining the total chemically combined nitrogen content of a sample, comprising the steps:

(a) decomposing said sample in one step in the presence of an oxygen-rich atmosphere of oxygen and an inert gas and at a temperature sufficiently above 700°C. that substantially all of the chemically bound nitrogen is converted to nitric oxide (NO), such decomposition being conducted in the absence of a catalyst,

(b) causing the nitric oxide produced by such decomposition to undergo a chemiluminescent reaction with ozone, and

(c) determining the magnitude of the chemiluminescent reaction to indicate the quantity of chemically combined nitrogen in said sample.

2. A method according to claim 1, wherein said temperature is in excess of 900°C.

3. A method according to claim 1 or claim 2, which includes the further step of chromatographically detecting constituents of the sample prior to decomposing the same and thereafter determining the chemically bound nitrogen content of the sample as aforesaid.

4. A method according to Claim 3, wherein the sample contains elemental nitrogen as well as chemically combined nitrogen, and wherein the elemental nitrogen content in the sample is chromatographically determined prior to decomposing the sample, whereby the total nitrogen content of the sample may be computed.

5. A method according to any preceding claim, wherein the magnitude of the chemiluminescent reaction is determined within the range of 600 to 900 nanometers.

6. A method according to any preceding claim wherein, prior to step (b), the mixture of nitric oxide and inert gas formed in step (a) is dried to lower the dew point thereof to below the temperature at which step (b) is conducted.

7. A method according to any preceding claim, wherein the inert gas is helium.

8. A method for determining the total chemically combined nitrogen content of a sample, according to Claim 1 and substantially as described with reference to Fig 1, Fig 2, or Fig. 3 of the accompanying drawings.

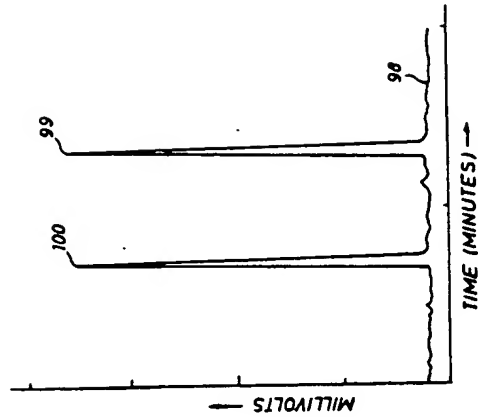
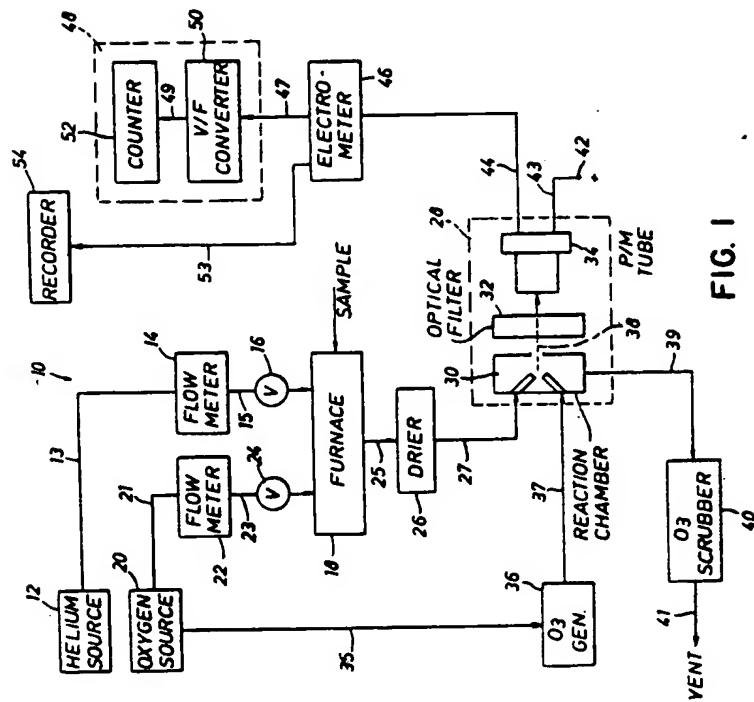
9. Apparatus for determining the total chemically combined nitrogen content of a sample, comprising:

a furnace having an inlet for receiving a sample to be analysed and connected to sources of oxygen and an inert gas whereby substantially all of the chemically bound nitrogen in the sample can be decomposed in the furnace in the presence of an oxygen-rich atmosphere of oxygen and an inert gas to nitric oxide (NO);

a reaction vessel communicating with said furnace to receive the nitric oxide-containing decomposition product therefrom and communicating also with a source of ozone for
5 chemiluminescent reaction with the nitric oxide received in the reaction vessel; and
chemiluminescent measuring means for determining the magnitude of a chemiluminescent reaction occurring in the reaction vessel to indicate the quantity of chemically combined
10 nitrogen in said sample.

10. Apparatus for determining the total chemically combined nitrogen content of a sample, according to Claim 9 and substantially as hereinbefore described with reference to Fig. 1, Fig. 2, or Fig. 3 of the accompanying drawings. 15

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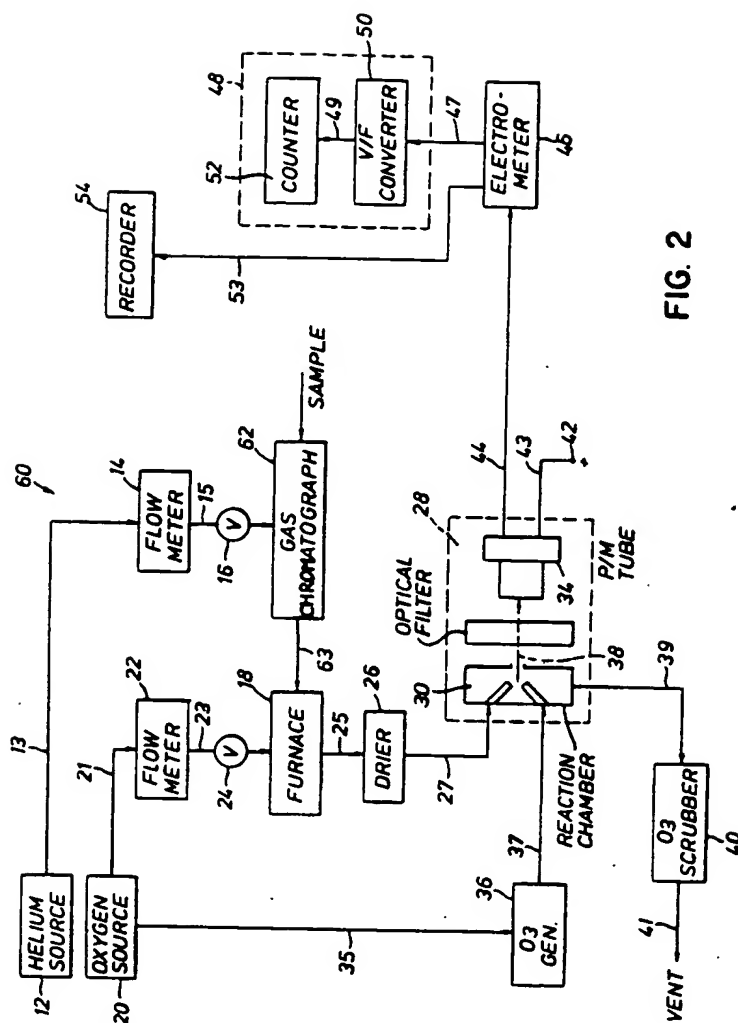


FIG. 2

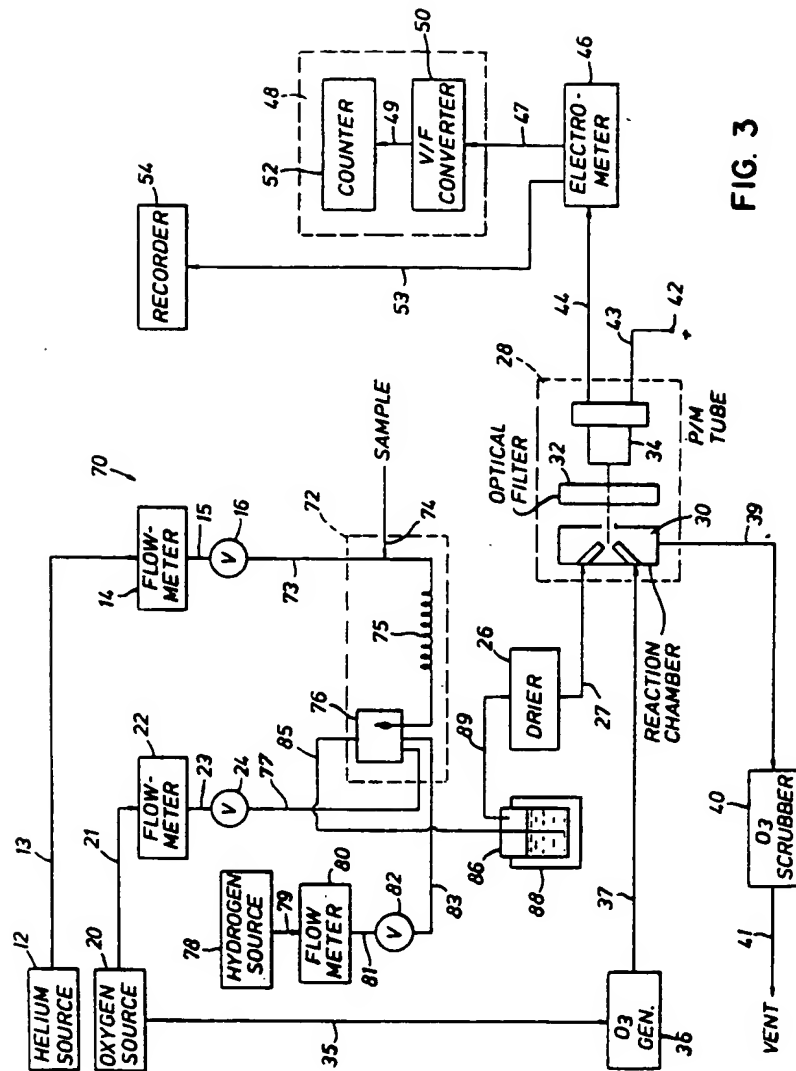


FIG. 3

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COMPLETE SPECIFICATION

4 SHEETS

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the Original on a reduced scale
Sheet 4

FIG. 4

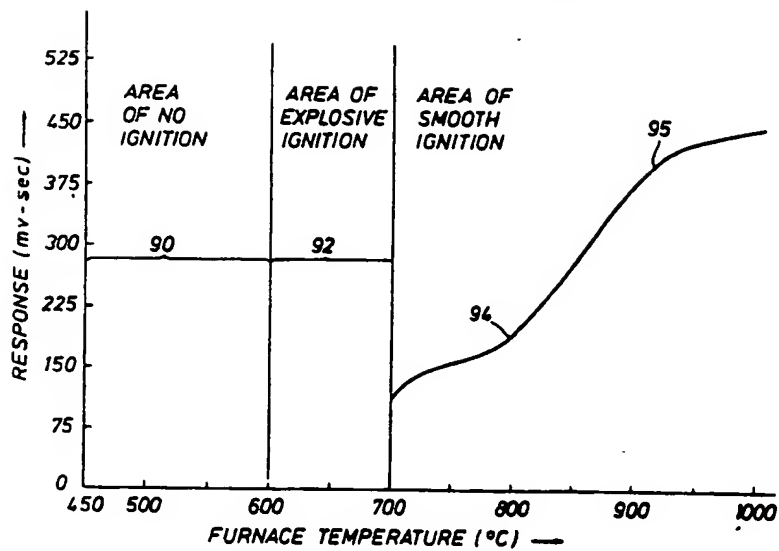


FIG. 5

